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SUBSTRATE AND SUPERSTRATE DESIGN MADE WITH
ETHYLENE-VINYL ACETATE AS POTTANT MATERIAL
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Modelling of Photodegradation in Solar Cell Modules

of Substrate and Superstrate Design Made with

Ethylene-Vinyl Acetate as Pottant Material

ANNUAL REPORT -- 1982



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ABSTRACT

We have developed earlier a computer model which simulates, in principle, the chemical changes in the photooxidation of hydrocarbons using as input data a set of elementary reactions, corresponding kinetic rate data and appropriate initial conditions.

During the past year we have further refined the model and exploited it to examine more closely the photooxidation and photostabilisation of a hydrocarbon polymer. The new results lead us to the following observations:

1. The time to failure, τ_f (chosen as the level of 5% C-H bond oxidation which is within the range we would anticipate for marked change in mechanical properties) varies as the inverse square root of the light intensity. However, τ_f is almost unaffected by both the photoinitiator type and concentration.
2. The time to failure decreases with the rate of abstraction of C-H by peroxy radicals but increases with the rate of bimolecular radical termination controlled by diffusion.
3. Of the various stabilisation mechanisms considered, the trapping of peroxy radicals is distinctly the most effective, although the concomitant decomposition of hydroperoxide is also desirable.
4. For a partially crosslinked polymer where the physical properties are not steep functions of crosslink density, it is unlikely that there will be dramatic failure modes due to net changes in molecular weight of the polymers.
5. Energy loss (power loss) due to polymer light absorption (with yellowing discoloration) will not be a significant failure mode.
6. Since the all-important peroxy radicals terminate by bimolecular disproportionation, at low concentrations they could have lifetimes of up to several hours, which would affect the extent of dark reactions in the daily cycle during outdoor applications.

Further work in the coming year will include more refinements to approach encapsulation grade EVA and thermal considerations.

I. INTRODUCTION AND OBJECTIVES

The JPL Flat-Plate Solar Array (FSA) Program has identified a number of possible configurations for modules containing silicon solar cells suitable for construction of a solar energy generating station and also for small-scale applications involving the use of solar-generated electricity. Although it appears possible now to meet many of the original design criteria for the cost of the components of these modules, a most critical feature of the design is that the components must maintain their integrity and function for a minimum efficiency equivalent to 20 years in an outdoor environment which features strong solar UV intensity.

To date, a number of failure and degradation modes have been identified. These include:

- | | |
|--------------------------------------|------------------------------------|
| 1. Soiling | 6. Electrical insulation breakdown |
| 2. Cell cracking/hot spots | 7. Encapsulant thermal degradation |
| 3. Interconnect fatigue | 8. ENCAPSULANT PHOTODEGRADATION |
| 4. Structural failure/glass breakage | 9. Delamination |
| 5. Electrical terminal failure | 10. Corrosion |

Any attempt to develop a technology for producing low-cost, long-life photovoltaic modules and arrays must therefore come to terms with the weathering effects experienced by the materials exposed to the sun's ultraviolet, oxygen, moisture and the stresses imposed by continuous thermal cycling, among other things. Polymeric substances which could find application as convenient protective covers, potants/adhesives and backcovers undergo slow, complex photooxidation which changes the chemical and physical properties of these materials. Absorption of the ultraviolet in the tail of the solar spectrum can cause the breaking of chemical bonds, resulting in embrittlement and increased permeability, or to crosslinking which can produce shrinking and cracks. In addition, oxidation often leads to discoloration and reduced transparency, and to the formation of polar groups which could affect electrical properties.

Much work has already been done to unravel the complexities of photooxidative processes and to develop some highly effective light (UV) stabilizers which can delay the onset of polymer embrittlement. Excellent reviews have been presented recently.¹ Some polymer systems have also been exploited to fabricate plastics with controlled lifetimes in the short range.^{2,3} However, very little is known about the ultimate changes that occur in polymeric substances after very long periods such as the 20-year regime appropriate for economic photovoltaic power plants.

There is no good way to predict the rates of the chemical and/or physical changes which occur from accelerated tests. In part, the problem has been that there is no adequate laboratory method to measure these effects over such extended times. Furthermore, accelerated tests (in which materials are exposed to higher intensity UV sources in controlled atmospheres) are of limited value in predicting rates since there is often no reciprocity between intensity and time of exposure.

A new procedure has been adopted in this work directed to developing for the first time, a reliable predictive capability for the lifetime of plastic components, particularly in solar energy modules. The procedure includes the following steps.

1. Identification of failure mechanisms of plastic components of the modules.
2. Determination of the chemical or physical causes of these mechanisms.
3. Development of precise analytical procedures to detect these chemical or physical changes at an early stage.
4. Construction of a computer model using a series of elementary rate equations to describe the chemistry and physics of these changes.
5. Validation of the mathematical model by comparison of data from real but well defined accelerated photochemical systems.
6. Prediction of actual performance lifetime by means of real-time monitoring of early degradation in appropriate outdoor locations and, using the computerised simulation, extrapolation to very much longer times.

Other workers in the FSA project have done ranking studies to select optimal material systems which should have tolerable levels of degradation in 20-25 years and yet meet the other basic design criteria. Of the prime candidates selected as potential pottant materials, an encapsulant grade of a copolymer of ethylene-vinyl acetate (EVA, trade name ELVAX, from DuPont) has emerged as a front-runner beside the alternate poly(n-butyl acrylate) (PnBA). We have, therefore, selected EVA as the polymer for which this new predictive capability will be developed. However, the general method, once refined and demonstrated, should find wide application to a wide variety of synthetic materials where a large number of fundamental reactions gives rise eventually to macroscopic deterioration. Most importantly, this new approach should provide new insight and understanding of this complex photooxidation process which should prove invaluable in the design of new solutions to the problem of stabilisation of polymers.

II. THE COMPUTER PROGRAM

Numerical methods for the solution of any large set of coupled differential equations have been developed. The particular method originally due to Gear⁴ has been applied by Allara and Edelson for the pyrolysis of alkanes⁵ and later by others^{6,7} for similar processes. Smog formation and detailed small-molecule photochemistry have also been studied by these numerical simulations.⁸ Semi-quantitative prediction has been possible in these cases. However, our work is the first attempt to simulate photooxidation kinetics in the case of polymers.

The computer package necessary to generate concentration-time profiles from a mechanistic model of elementary reactions and rate data was completed

in the first two years. Our model now consists of a set of reactions (Table I) for the basic reaction sequence based on the now well established mechanism of hydrocarbon oxidation. Rate parameters have been assigned to these fundamental equations, based on our best estimates from the literature⁹ (Table I). The modified program calculates by stepwise integration in real time the varying concentrations of chemical species formed during photooxidation. To validate our numerical procedure we employed the data base given for the cesium flare system, and generated curves identical to those of Edelson¹⁰ for the same system. The excellent agreement between predicted and actual rate curves showed that the program itself (irrespective of the data base) performs in a satisfactory manner.

III. MECHANISM OF PHOTOOXIDATION

Amorphous Polyethylene

As a starting point for polymer photooxidation we have looked at amorphous high-density polyethylene where we presume that short-range diffusion rates in reaction centres should approach that of viscous liquids. In practice, many polymers will show only chemical changes in the hydrocarbon moiety since bond breakage will commonly take place initially in the more labile C-H and C-C bonds. Initiation will take place following UV absorption by ketone or hydroperoxide groups or even fortuitously by some C-H bond cleavage. The possibilities of energy transfer among different groups have also been included in the model. Propagation takes place via the formation of peroxy radicals followed by hydrogen atom abstraction from the backbone and repeated fast oxygen addition. Peroxy radical chain carriers terminate by disproportionation to form alcohols and ketones. Further photolysis of ketone products leads to another autocatalytic chain. The reduced set of important reactions considered and the best literature estimates of corresponding rate constants have been summarised in Scheme I.

Ethylene-Vinyl Acetate Copolymer

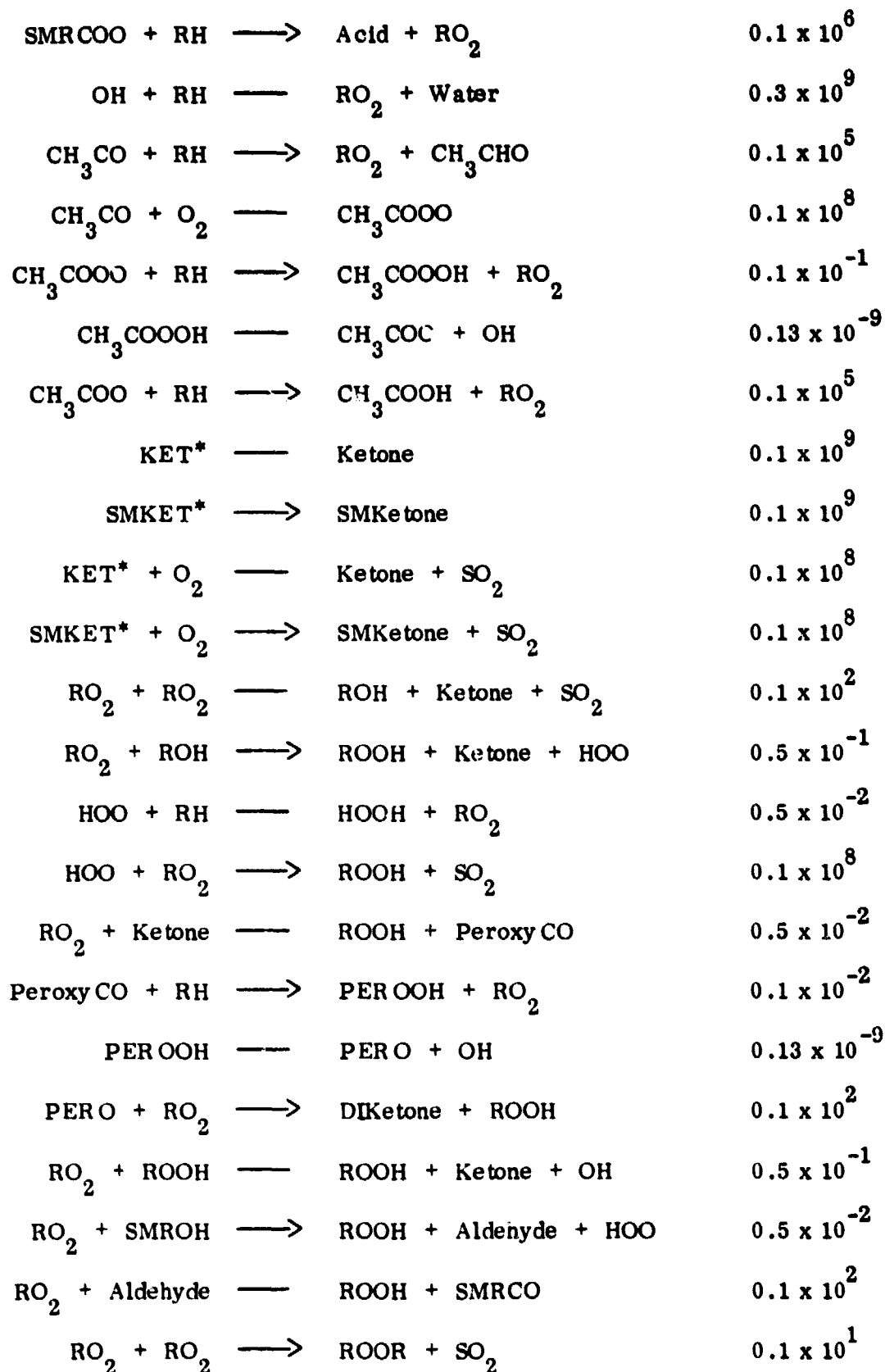
Several studies have been carried out on the thermal degradation,¹¹⁻¹³ thermal oxidation^{14,15} and photooxidation¹⁶ of EVA.

EVA thermally degrades in two stages. Scission of acetoxy groups occurs at 275 to 350°C in a manner similar to that of poly(vinyl acetate) (PVA) causing elimination of acetic acid and giving unsaturation by a molecular chain mechanism involving adjacent acetate units. The hydrocarbon chains of the polymer residue degrade above 400°C. Thus, thermal decomposition of the acetate groups in EVA can be assumed to be negligible at room temperature.

Thermal oxidation of EVA occurs mainly in the PE segments following the usual autocatalytic radical mechanism analogous to that of polyethylene. The

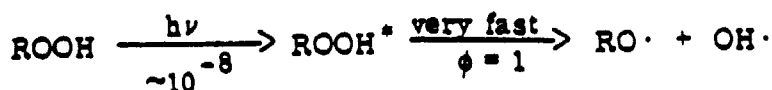
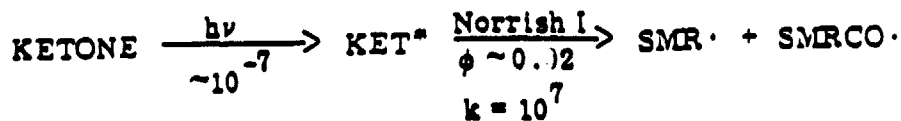
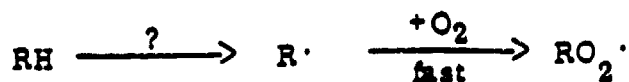
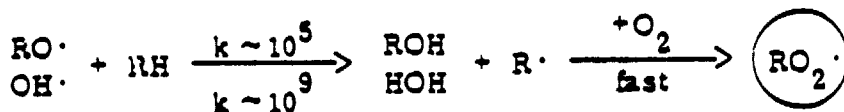
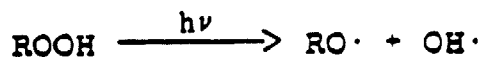
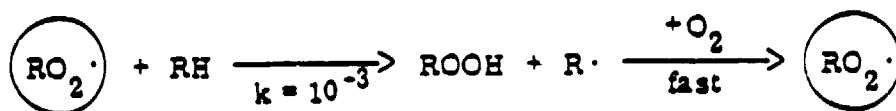
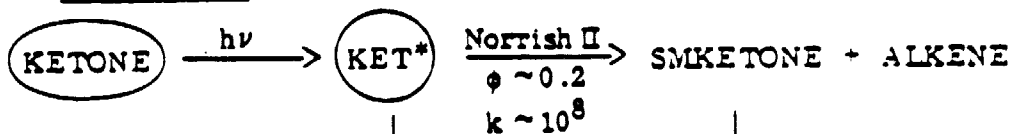
TABLE I. Elementary Reactions in Polymer Photooxidation and Corresponding Rates

Reaction matrix	Rates
Ketone \longrightarrow KET*	0.7×10^{-9}
KET* \longrightarrow SMRO ₂ + SMRCO	$0.2 \times 10^{+6}$
SMRCO \longrightarrow SMRO ₂ + CO	0.1×10^7
KET* \longrightarrow Alkene + SMKetone	0.2×10^7
SMKetone \longrightarrow SMKET*	0.7×10^{-9}
SMKET* \longrightarrow SMRO ₂ + CH ₃ CO	0.2×10^7
SMKET* \longrightarrow Alkene + Acetone	0.2×10^8
ROOH \longrightarrow RO + OH	0.13×10^{-9}
RO ₂ + RH \longrightarrow ROOH + RO ₂	0.1×10^{-2}
SMRO ₂ + RH \longrightarrow SMROOH + RO ₂	0.1×10^{-2}
SMROOH \longrightarrow SMRO + OH	0.13×10^{-9}
SMRO + RH \longrightarrow SMROH + RO ₂	0.1×10^6
RO + RH \longrightarrow ROH + RO ₂	0.1×10^6
RO \longrightarrow SMRO ₂ + Aldehyde	0.1×10^5
KET* + ROOH \longrightarrow Ketone + RO + OH	0.1×10^2
SMKET* + ROOH \longrightarrow SMKetone + RO + OH	0.1×10^2
SMRCO + O ₂ \longrightarrow SMRCOOO	0.1×10^8
SMRCO + RH \longrightarrow RO ₂ + Aldehyde	0.1×10^5
SMRCOOO + RH \longrightarrow SMRCOOOH + RO ₂	0.1×10^{-1}
SMRCOOOH \longrightarrow SMRCOO + OH	0.13×10^{-9}
SMRCOO \longrightarrow SMRO ₂ + CO ₂	0.1×10^5

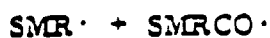
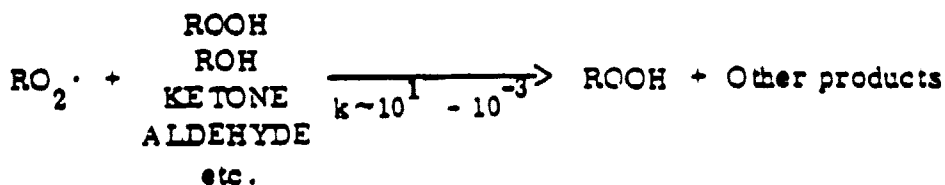
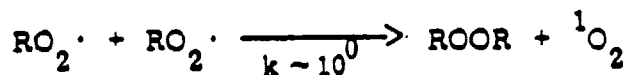
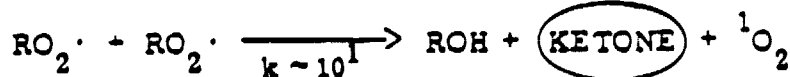


SO_2	\longrightarrow	O_2	0.6×10^5
$\text{SO}_2 + \text{Alkene}$	\longrightarrow	ROOH	0.1×10^4
$\text{RO}_2 + \text{Alkene}$	\longrightarrow	Branch	0.5×10^0
$\text{SMRO}_2 + \text{Alkene}$	\longrightarrow	ROOH	0.5×10^0
$\text{RO}_2 + \text{QH}$	\longrightarrow	$\text{ROOH} + \text{Q}$	0.1×10^7
$\text{KET}^* + \text{Q1}$	\longrightarrow	$\text{Ketone} + \text{Heat}$	0.1×10^7
$\text{ROOH} + \text{QD}$	\longrightarrow	PRODS	0.1×10^7

^a $[\text{O}_2] = 10^3 \text{ M}$ (constant); SMProduct = product from chain cleavage.

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OF POOR QUALITY**Initiation****Propagation**Peroxide chainKetone chain

$$\downarrow \text{Norrish I}$$

$$\phi \sim 0.02$$
**Termination**

Scheme I. Polyethylene photooxidation scheme.

accompanying thermal degradation of the vinyl acetate units results in the evolution of acetic acid and generation of unsaturation as mentioned previously. Subsequent oxidation of the unsaturation was reported to produce various carbonyl-containing compounds including aldehydes, ketones, esters and acids. Again, it is apparent that thermal oxidation will be limited to the PE moiety at ambient temperatures.

The photooxidation of EVA has been reported only by Lugova et al.¹⁶ employing UV irradiation in air at room temperature. Their work suggests that the oxidation of the ethylene units and the photoreactions of the acetate chromophores proceed independently of each other, essentially in a parallel fashion.

The above results indicate that a generalized mechanism of photooxidation of EVA can be constructed using the known polyethylene photooxidation mechanism as a model for reactions expected to occur in the hydrocarbon portion of EVA. Similarly, information can be extracted from studies of the photooxidation of PVA and of acrylate polymers which allows formulation of the fundamental photochemical processes expected for the acetate groups in EVA. Some modifications to the present model for polyethylene will therefore be necessary to allow for the differences due to substitution in EVA.

IV. COMPUTER MODELING RESULTS AND DISCUSSION

Photooxidation of Amorphous Polyethylene

Figure 1 shows the general behavior of amorphous polyethylene on exposure to different intensities of UV light. Assuming initiation by 10^{-3} M ketone groups and constant ambient oxygen pressure, the model shows that the C-H bonds become oxidised slowly at first and then more rapidly later on. We have used the level of 5% C-H bond oxidation to assign a point of failure which is within the range we would anticipate for marked change in mechanical properties. Under typical conditions the time to failure (τ_f) of the neat polyethylene would be three to four months. Product formation and other observations are consistent with our experimental knowledge of PE weathering.¹⁷ The only exception is the high yield of hydroperoxide which we are unable to eliminate in our model predictions and which may point to the inadequacy of experimental methods for monitoring -OOH groups in oxidised films without further modification. The time to failure is plotted as a function of the intensity of light in Figure 2 where we find the relationship that $\tau_f \propto I^{-1/2}$, as one would expect for photochemical initiation producing two radical species.

Also, we find that the behavior is almost unaffected by both the initiator type and concentration (Figure 3). This is not surprising for an autocatalytic process since the result is dominated by relative rates of propagation and termination.

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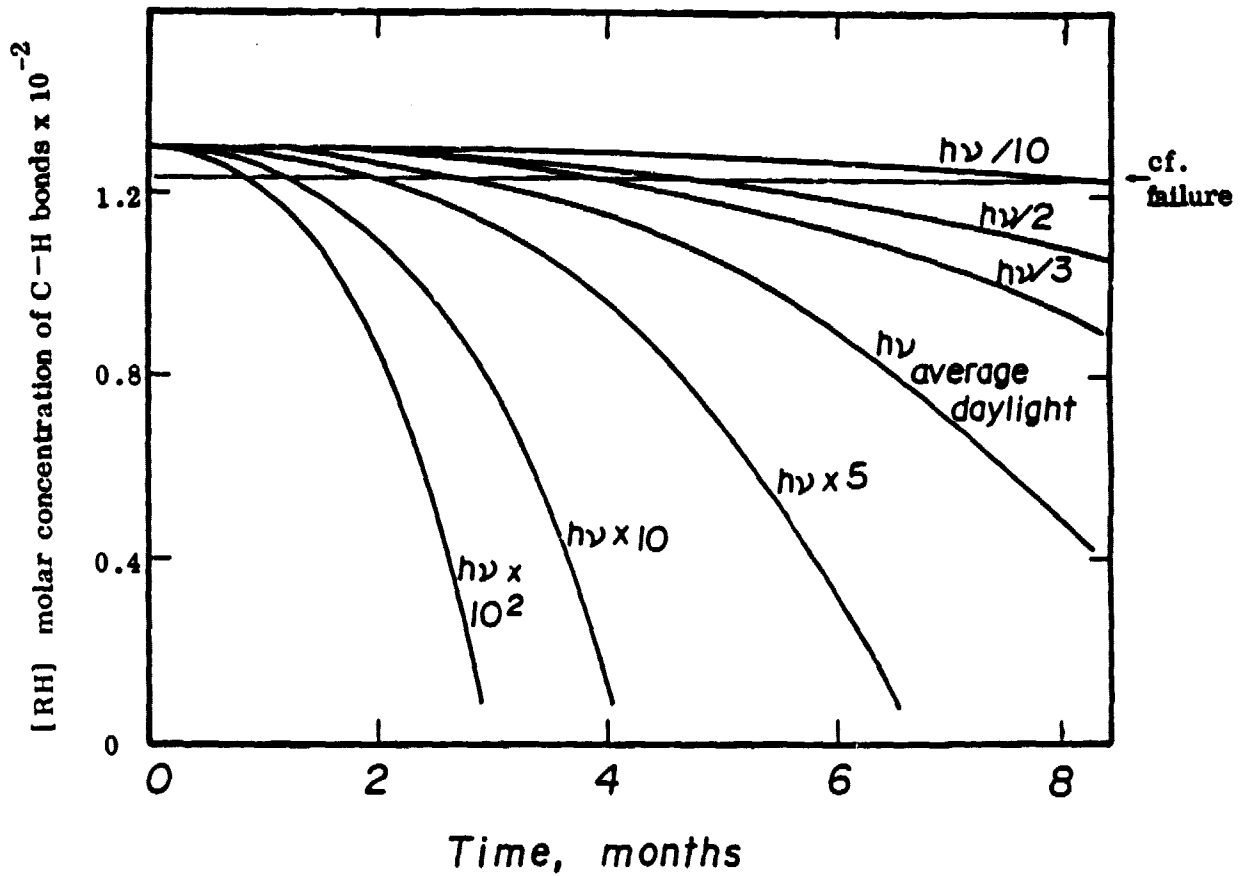


FIGURE 1. Photooxidation of unstabilized PE. Time to failure varies with light intensity.

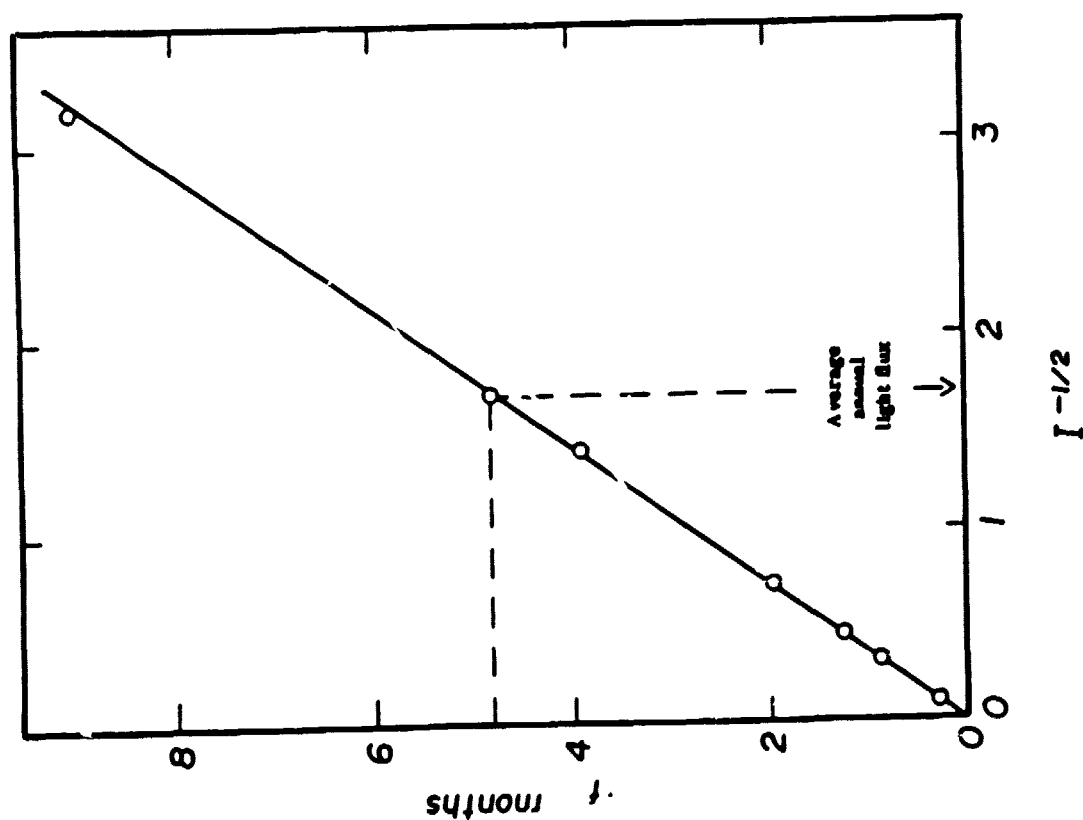


FIGURE 2. Photooxidation of unstabilized PE.
Time to failure as a function of light intensity.

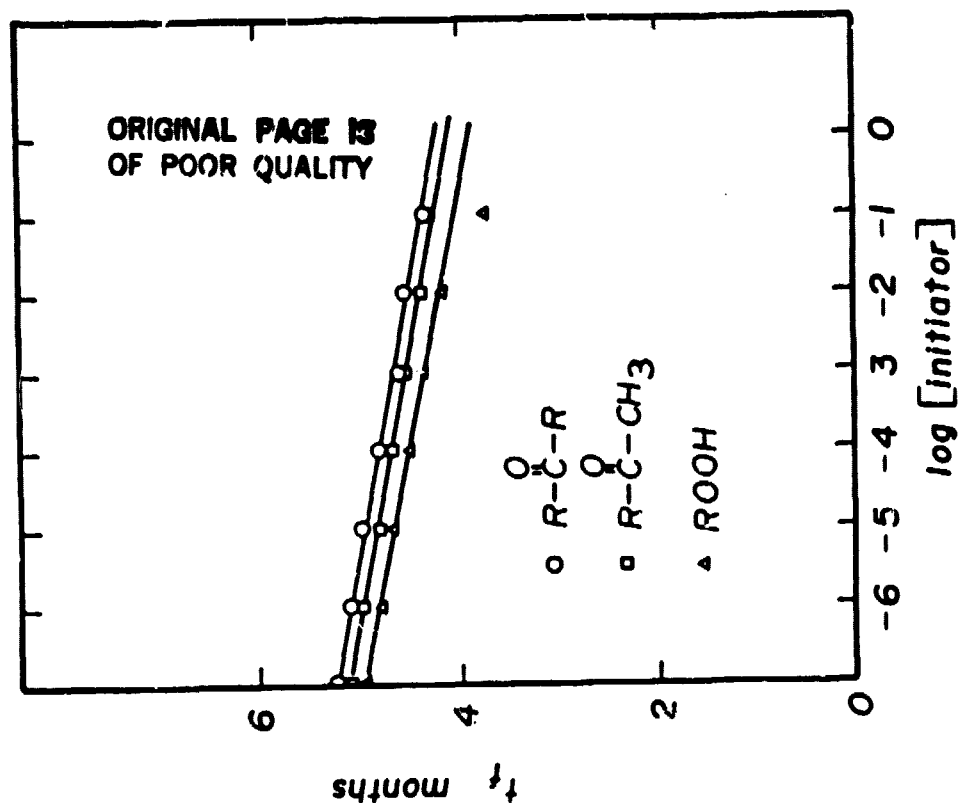
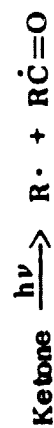


FIGURE 3. Photooxidation of unstabilized PE.
Time to failure as a function of initiator type
and concentration.

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Two conclusions can be drawn. First, there has been much heat generated in the literature about the relative importance of the various possible mechanisms for initiation (ketone groups, hydroperoxide, catalyst residues, singlet oxygen) but the controversy is practically irrelevant if initiation does not much influence the course, rate or extent of photooxidation. Second, in terms of stabilisation, minute amounts of photoinitiation will lead to practical failure so that the purification of polymers to minimise the initiating residue is not a practical alternative for stabilisation.

Figure 4 shows the dependence of the time to failure on the rate of propagation, i.e., the rate of hydrogen abstraction from the polymer backbone. The log-log plot is linear with a negative slope less than unity. The rate of abstraction of $^t\text{C}-\text{H}$ as in vinyl acetate segments (30%) of EVA, would only be a factor of two to three higher than for $^s\text{C}-\text{H}$ as in PE. The time to failure in EVA should therefore not be very different from PE. (The rate for polypropylene is enhanced by the presence of sequences of $^t\text{C}-\text{H}$ allowing extensive intramolecular hydrogen migration, hydroperoxide sequences and subsequent reactions.)

Figure 5 shows the dependence of the time to failure on the rate of bimolecular radical termination which is directly related to diffusion of the polymeric segments in the solid matrix. Again the log-log plot is linear with a positive slope this time, again less than unity. Increased diffusion shortens the kinetic chain length and increases the time to failure.

The Effect of Diffusion on Chemical Degradation

In principle, diffusion in a polymer matrix will affect the rates of all the bimolecular reactions to some degree or another. We have treated four categories of such reactions.

1. Small molecule-small molecule reactions. These reactions are almost non-existent in the mechanism except for the addition of oxygen to small radical fragments such as the acyl radical from type I cleavage of methyl ketones. The relatively high solubility of oxygen and the mobility of these small molecules in a medium that is essentially equivalent to a very viscous liquid in local regions, minimises any special "polymer effect". The other stable small molecule product is water which may have effects on electrical properties but does not participate in the photooxidation sequence per se.

2. Small molecule-polymer "moiety" reactions. Groups formed on the backbone of polymer chains (such as $\text{ROO}\cdot$ peroxy, RCO keto, $\text{RO}\cdot$ alkoxy, etc.) do react with "small molecule" species including oxygen and some radical fragments. The effect of the polymer medium apparently is to reduce the bimolecular collision (reaction) rates by a factor of about 10^{-2} relative to fluid solution rates, due to the reduced mobility of the chains.

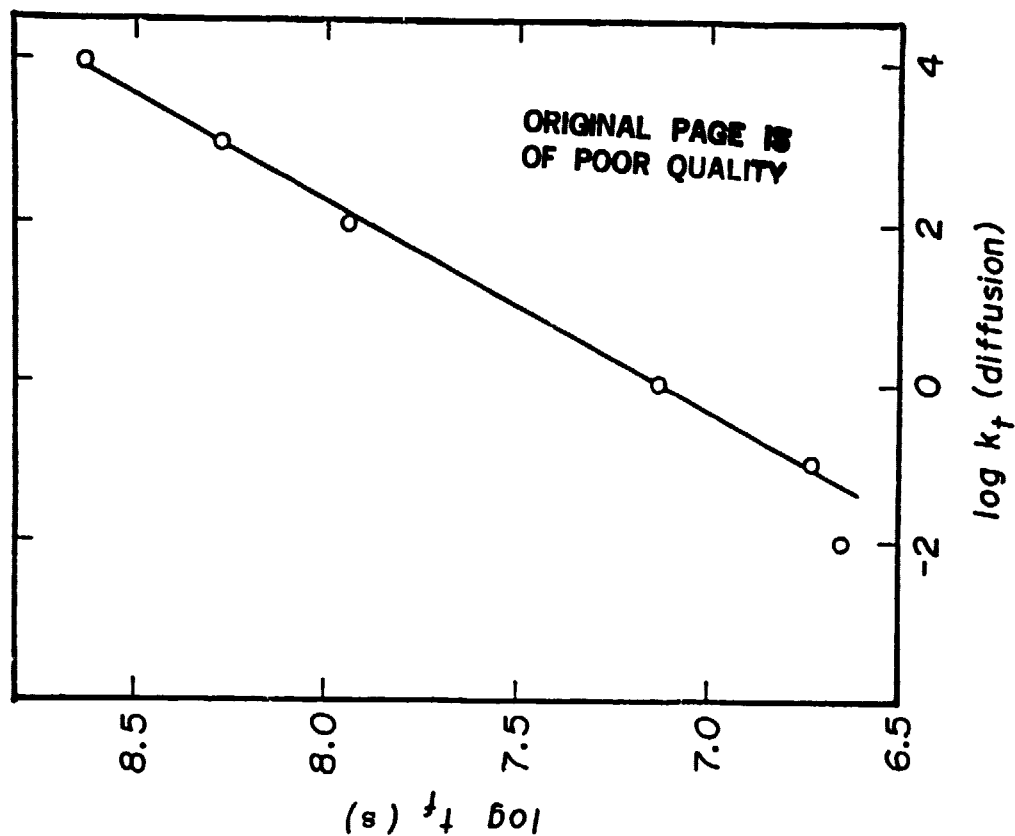


FIGURE 5. Photooxidation of unstabilized PE. Effect of bl(macro) molecular diffusion (radical termination on time to failure, e.g.,

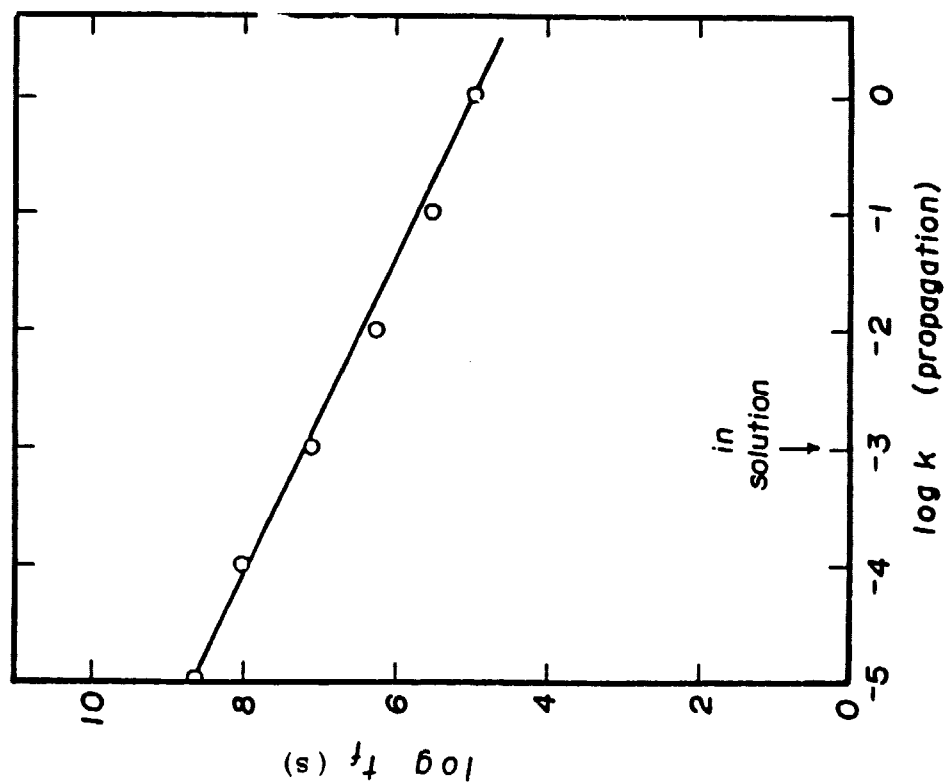
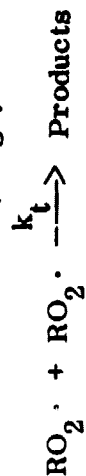


FIGURE 4. Photooxidation of unstabilized PE. Time to failure as a function of propagation rate constant.



3. Small molecule-polymer "solvent" reactions. Many radical reactions involve H-atom abstraction from the hydrocarbon backbone of the "solvent" polymer matrix. It is likely that all species will have C-H bonds in the immediate vicinity so that there would be no real sensitivity to diffusion and rates would then be similar to fluid solution rates.

4. Polymer "moiety"-polymer "moiety" reactions. Chemical groups formed on the backbone of polymer chains such as peroxy radicals, hydroperoxides, ketones, etc. can undergo bimolecular reactions such as disproportionation, energy transfer etc. The effect of the polymeric medium apparently is to reduce the bimolecular rates by a factor of about 10^{-4} relative to fluid solution rates, due to the reduced mobility of both reactants.

What we have shown in Figure 5 is that increasing the rates of all the bimolecular reactions, proportionately and together, causes a net increase in the induction time (time to failure). This result probably reflects the importance of the bimolecular termination of polymeric peroxy radicals which can then compete more effectively with the hydrogen abstraction propagation step, when diffusion is increased.

The Effect of UV Stabilisers and Antioxidants

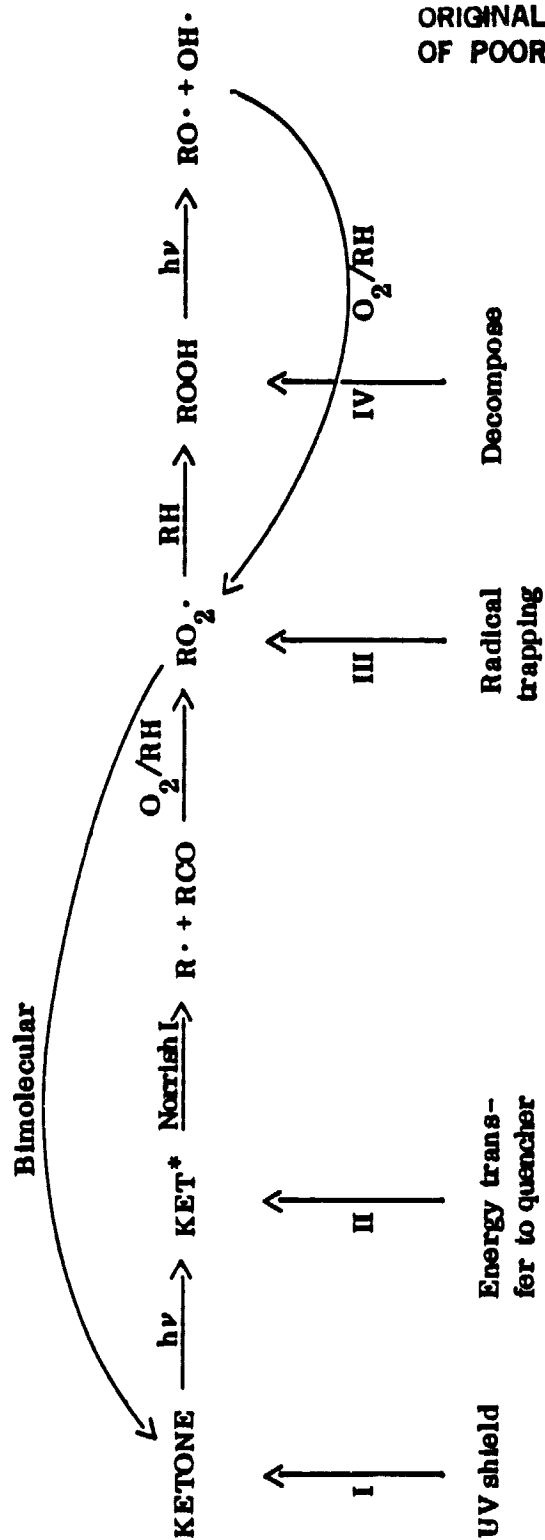
Scheme II represents the overall scheme of photooxidation and the various categories of stabilisation mechanisms. We have examined each in turn.

1. UV shield. Effective stabilisation of pottants or cover sheets by UV shielding would require absorption by an additive of incident radiation at wavelengths below (and only below) the visible (for colorless systems), high concentrations (several weight percent for adequate coverage), and chromophores of high extinction coefficient ($> 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in very thin films. The additive must be capable of harmlessly dissipating the substantial quantities of absorbed energy without being destroyed itself and without sensitisation of oxidation. This is the principal mode of stabilisation used at present in the addition of substituted hydroxy benzophenones to EVA (cf., Springborn formulations).

2. Energy transfer to quencher. We added a reaction to allow dissipation of the excited ketone with a rate constant comparable to the upper limit for a small molecule diffusion in a polymer matrix.



Figure 6 shows that up to 1M concentration ($\sim 8\%$) of quencher had minimal effect on the induction time. Such a bimolecular process is just too slow for the fast unimolecular reactions of the excited ketone and stabilisation is ineffective. Again it would seem that this method per se would not be appropriate for the solar cell modules.



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Scheme II. Stabilisation mechanisms

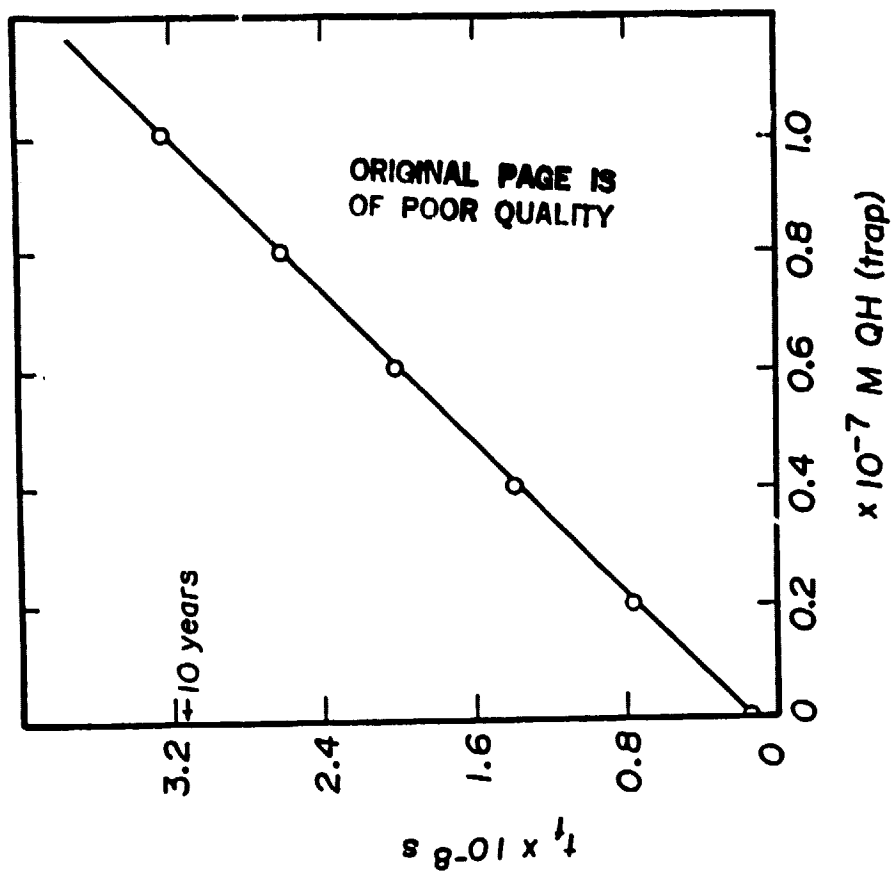


FIGURE 7. Stabilization of PE by radical trapping (very low molecular concentration).

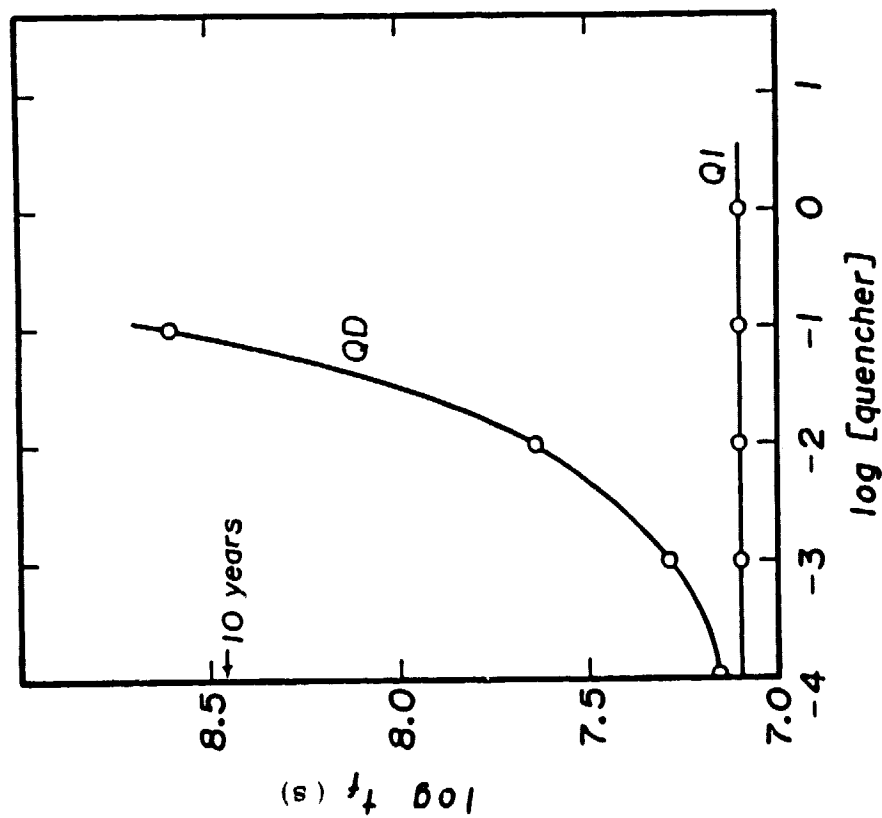
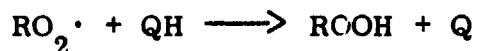


FIGURE 6. Stabilization of PE.



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3. Radical trapping. Addition of a radical trap which functions much the same as in thermal oxidation by scavenging of reactive radicals has proved quite effective.



For the same value of rate constant as in (2) and for concentrations as low as 10^{-7} M, the photooxidation process was slowed. Figure 7 shows the linear dependence of the induction time as the concentration of QH is altered. Note that the trap is consumed in the process and the apparent induction time is associated with its removal. The stabilisation is less effective for higher intensity because the faster photo- or thermal-decomposition of ROOH continues the degradation process.

4. Decomposition of the hydroperoxide. Addition of the reaction



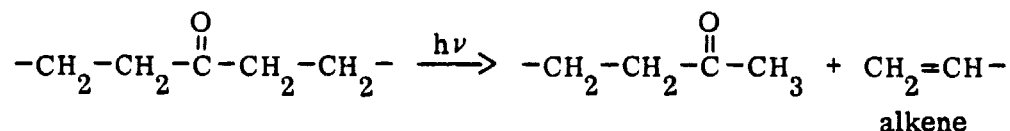
does prove effective in stabilisation since it interrupts the autocatalytic chain. Figure 6 also shows the effect on a log-log scale which is systematic but not linear.

We therefore anticipate optimum photoprotection for the encapsulant grade polymers from a combination of methods (3) and (4) above. Some nickel chelates have been known to function in both ways and ought to be considered as candidates for FSA applications. Further simulations will be continued as we attempt to approach a real life "encapsulation grade" EVA material in the coming year.

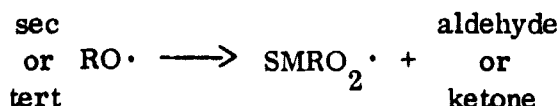
Material Consequences of Photooxidation

We have during the year begun to monitor the model predictions regarding possible "failure" mechanisms: wrinkling, embrittlement, etc. (as a result of crosslinking and/or scission), discoloration and other effects (due to buildup of unsaturated groups) in the polymers.

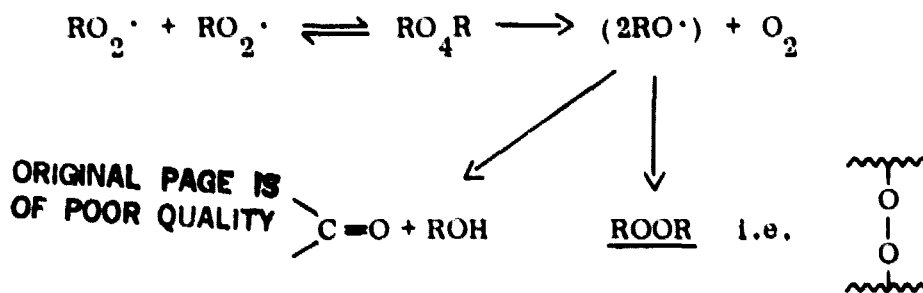
1. Molecular weight changes. In our model we account for scission of polymers by the Norrish type II process:



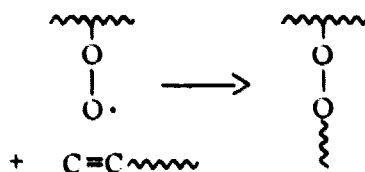
and by the less important β -processes:



Likewise, crosslinking is accounted for by the Russell mechanism for peroxy radical termination:



and by the addition of peroxy radicals to the alkene ends formed in the Norrish type II process:



Figures 8, 9 and 10 show the changes in alkene, ROOR crosslinks and branch products, respectively, as a function of time with and without stabilisers. Assuming a density of 0.9 and a molecular weight of 100,000 for the polymer, our calculations suggest that at 10% RH oxidation, about 6% of the polymer molecules have branch points, whereas about 2% have ROOR crosslinks and somewhat less have undergone cleavage to form the alkene. Since the concentration of branch points is highest, the model does account for the net effect of an increase in molecular weight.

To make more quantitative estimates of changes in average molecular weights, crosslink densities or gel dose, we need more information on molecular weight distribution which is not available at the present time.

However, the model does suggest that for a partially crosslinked polymer where the physical properties are not steep functions of crosslink density, we are unlikely to find such changes as an important failure mode in FSA applications, especially if we effectively arrest the photooxidative processes with appropriate stabilisers.

2. Discoloration. It is commonly observed that extensive photooxidation leads to discoloration ("yellowing") of hydrocarbon polymers. We account for this in our mechanistic model by a series of reactions leading to the formation of diketone:

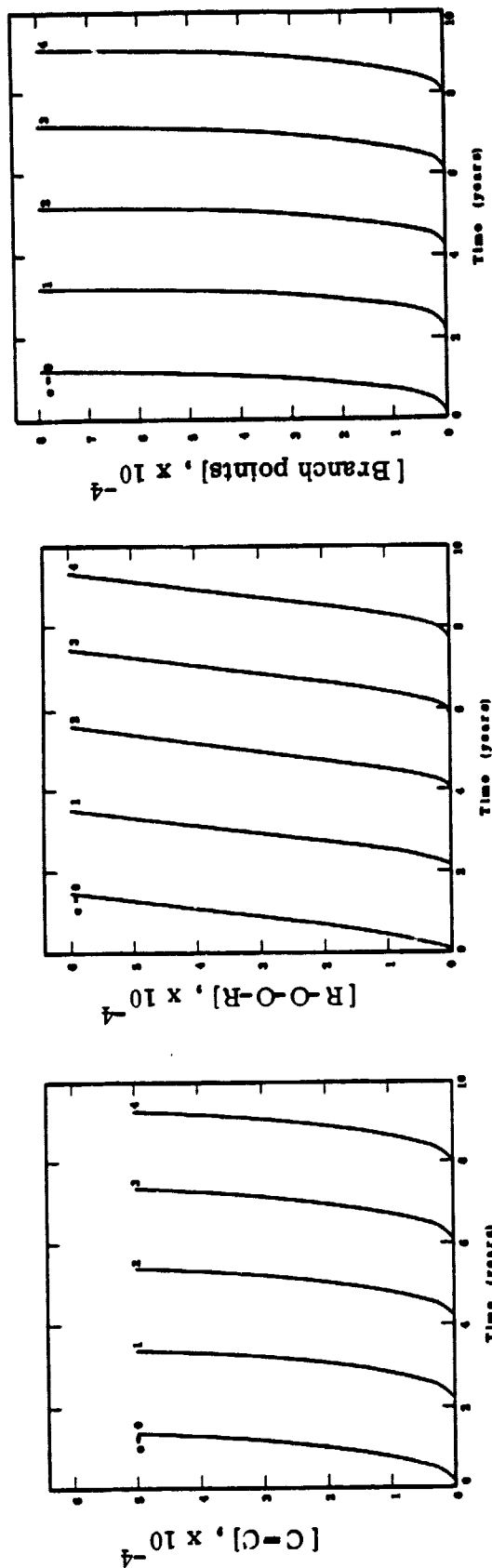
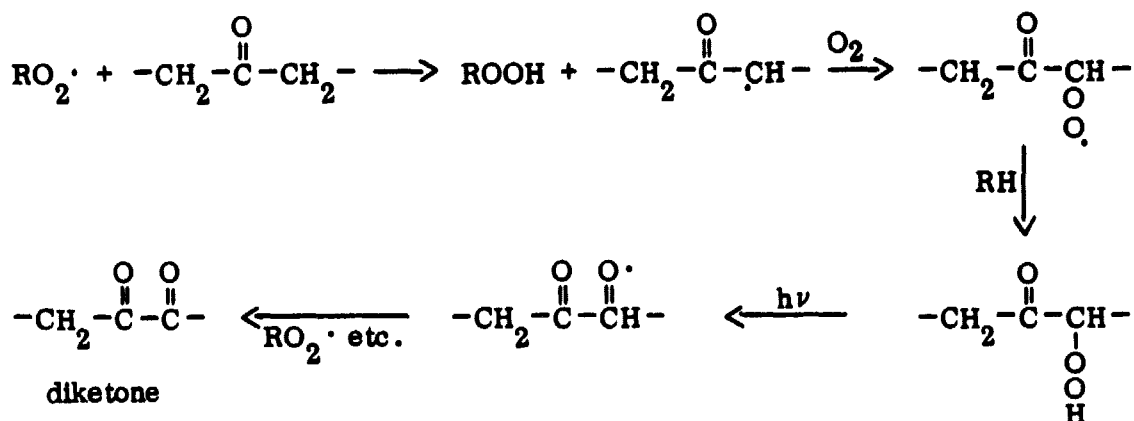
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FIGURE 8. Effect of stabilizer on alkene formation. Stabilizer concentration, c ($\times 10^{-6}$ wt-%).

FIGURE 9. Effect of stabilizer on formation of crosslinks. Stabilizer concentration, c ($\times 10^{-6}$ wt-%).

FIGURE 10. Effect of molecularly dispersed stabilization on formation of branch points. Stabilizer concentration, c ($\times 10^{-6}$ wt-%).



The absorption spectrum of the diketones (cf. biacetyl in Figure 11) shows absorption in the blue-violet region leading to a yellow color. Model calculations give us the change in absorbance (maximum) for a 0.1 cm film during extensive photo-oxidation (Figure 12). The net effect is that about 0.1% of the light is absorbed at the peak after 5% oxidation and less than 0.5% even at 30% oxidation levels (i.e., cf. RH removal). It is known that about 10% of solar energy lies in this region of diketone absorption (400 - 450 nm). This means that less than 0.01% of energy loss will occur due to yellowing up to 5% oxidation.

We have concluded from the model that if only diketone is responsible for the yellowing effect, then the energy loss (power loss) due to polymer light absorption will not be a significant mode of failure for photovoltaics in FSA applications.

Further Observations

1. Model stabilisers. Our results to date have suggested that the "ideal" stabiliser for the polymers in photovoltaic applications might best function as peroxy radical traps and also as hydroperoxide decomposers. The stabiliser would also be photostable itself and highly compatible with the polymers for efficient dispersion during formulation. Some Ni(II) chelates (such as Ni(II) di-n-butylthiocarbamate) and substituted benzophenones (such as 2-hydroxy-4-dodecyloxybenzophenone) may be good candidates.

For effective stabilisation to 20 years, our model suggests that a molecular concentration of 10^{-5} M would be adequate. This corresponds to 10^{-5} wt-%, assuming a molecular weight of about 400 for the stabiliser. The model results to date show that for each 1×10^{-6} wt-% of stabiliser the time to failure increases by two years systematically. In typical commercial practice, stabiliser loadings are much higher (0.1 - 1% and even higher for polyolefins), possibly because of the inability to formulate such a stabilizer.

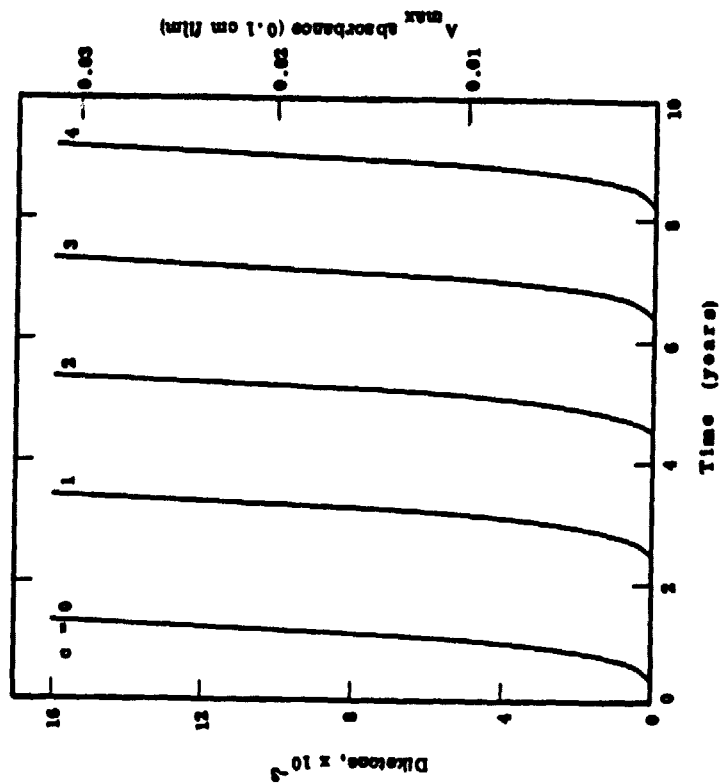


FIGURE 12. Effect of molecularly dispersed stabilizer on diketone formation. Stabilizer concentration, c ($\times 10^{-6}$ wt %).

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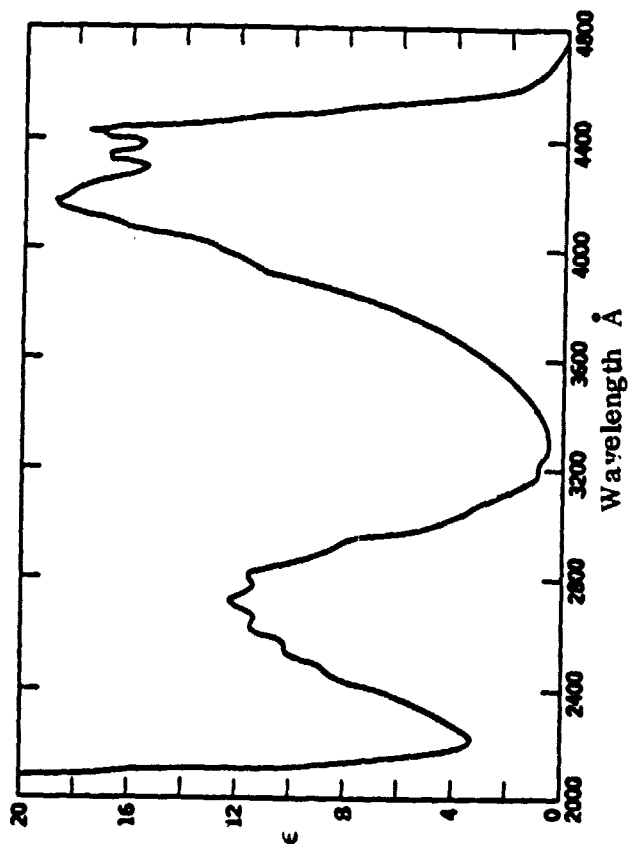


FIGURE 11. Absorption spectrum for bi-acetyl $[\text{CH}_3\text{COCOCH}_3]_2$, 25° .

2. The lifetime of peroxy radicals. We looked at the decay of peroxy radicals in the dark by removing all photochemical steps from our reaction sequence. The decay is bimolecular and we monitored the time to decrease to one-third the original value $[RO_2\cdot]$ as a function of the latter. The results show a linear inverse dependence with lifetimes up to many hours (Figure 13). We expect to follow this up and reproduce theoretically some of the recent experimental results on the ESR decay studies of peroxy radicals in polymers done by Dr. Amitava Gupta and his colleagues at JPL. This may provide an excellent verification probe of our model to increase the level of confidence in its predictions.

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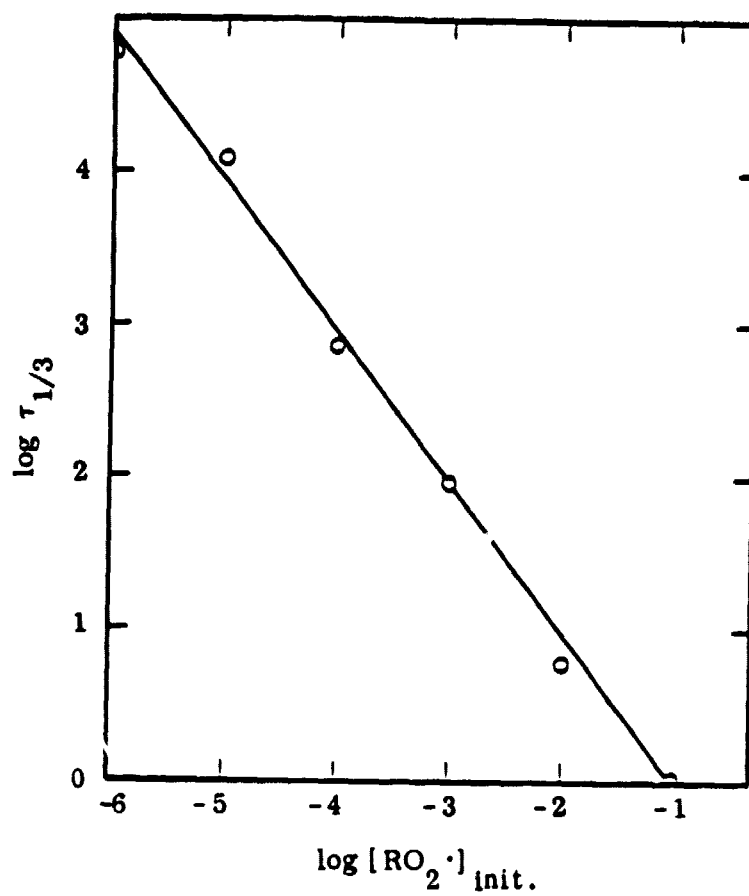


FIGURE 13. Lifetime of peroxy radicals in the dark.
($\tau_{1/3}$ in sec)

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